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Experimental Measurement of Vapor–Liquid Equilibrium in Alcohol/Water/Salt Systems

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Vapor–liquid equilibrium measurements have been performed on a set of alcohol/water/salt solutions at atmospheric pressure with a modified Othmer still and a modified Boublík–Benson still. The systems studied are methanol and water with NaCl, NaBr, KCl, and KBr; 1-propanol and water with NaCl, KBr, and NaBr; and 2-propanol with water and NaBr. The measurements are for salt concentrations ranging from infinite dilution to saturation for each water/alcohol solvent mixture. These experimental results constitute part of a database being developed to test theoretical models of mixed-solvent–electrolyte systems.

1. Introduction

A mixed-solvent electrolyte system consists of an electrolyte (such as a salt) dissolved in a solvent that is a mixture of two or more nonelectrolyte species (such as alcohol and water). Such systems have been the subject of intense research for a century, and the experimental and theoretical literature related to these systems is voluminous, as is evidenced by the thorough reviews of Furter (*1*, *2*) and the diversity of papers published in two American Chemical Society symposium volumes (*3*, *4*) devoted to the subject.

Mixed-solvent electrolytes are important because they arise in many naturally occurring systems (such as brine-containing oil reservoirs and biological fluids) and as intermediates or products in many industrial processes. A significant portion of the industrial interest in mixed-solvent electrolytes arises from their potential application in extractive distillation. When a nonvolatile salt is added to a nonelectrolyte mixture, the relative volatility of the nonelectrolyte species is altered. For example, suppose a strong electrolyte (3) such as potassium acetate or sodium chloride (which dissociate to form $K^+/C_2H_3O_2^-$ and Na^+/Cl^- ions, respectively) is added to an ethanol (2)/water (1) solution. The conventional qualitative picture is that the ions preferentially complex with the water molecules, creating a high molecular weight species that, compared to the salt-free case, has lower vapor pressure relative to the ethanol. Thus, the relative volatility of ethanol, defined by

$$\alpha_2 = \frac{y_2/x_2}{y_1/x_1} \tag{1}$$

where x_i and y_i are respectively the liquid- and vapor-phase compositions of species *i* at equilibrium, is increased by the addition of salt. Even at very small concentrations of these salts, this increase in volatility is sufficient to eliminate the azeotrope at 95 mol % ethanol, suggesting that salt may be a useful mass separating agent for extractive distillation. This alteration of phase equilibria in nonelectrolyte mixtures due to the presence of salt is known as the "salt effect", and the component with increased volatility is said to be "salted out" while the other component is said to be "salted in".

The salting out of alcohol from aqueous solutions has been recognized and exploited commercially at least since the twelfth century when Italian vintners discovered that the addition of salt to water/ethanol mixtures yielded higher concentration alcohol solutions upon distillation (*5*, *6*). However, there are many other important azeotropic systems that can be separated via extractive distillation using salts as the separating agent (*1*, *2*). Compared to an extractive distillation using a liquid mass separating agent, the use of salt requires that the salt enter the distillation column by dissolution into the reflux stream since the nonvolatile salt remains entirely in the descending liquid phase. If the salt is not introduced through the reflux stream, at several plates vapor would be in contact with salt-free liquid. Thus, the applicability of extractive distillation is restricted somewhat by the solubility of the salt in the reflux stream.

If the salt is fed at a constant rate to the reflux stream of a continuous distillation column operating at steady state (assuming constant molar overflow), then the molar salt concentration in the liquid phase will remain constant throughout the rectifying and stripping sections of the column despite progressive changes in solvent composition as the column is descended. Therefore, vapor–liquid equilibrium data required for column design should consist of T-x-y (where T is temperature) measurements at constant salt concentration. Recovery of the salt from the bottoms product for recycle operations is a simple evaporation operation.

Several authors (*7*, *8*) have evaluated the advantages and disadvantages of using salts as separating agents for aqueous nonelectrolyte systems. Discussion of these pros and cons is beyond the scope of the present paper; it is sufficient to note that where solubility relationships permit, extractive distillation by salt effect at least offers a viable alternative to presently used methods for difficult separations.

There are several separations that have proved economically favorable to perform using salt as the mass separating agent:

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for several years, the German firm Degussa licensed the HIAG process (9), using mixed acetate salts to separate ethanol/water mixtures. Between 1930 and 1950, over 100 such plants were built to produce anhydrous ethanol as a motor fuel extender. Cook and Furter (8) produced 99.9+ mol % anhydrous ethanol using 6 mol % potassium acetate as the separating agent in a 12-tray bubble-cap distillation column (representing reductions both in the amount of separating agent and the number of trays required as well as an increase in product purity compared to a typical extractive distillation process employing a liquid separating agent such as benzene). Furter (2) records other efforts by researchers in Japan and the Soviet Union to research and develop alcohol/water extractive distillation systems employing the salt effect. Sloan (10, 11) describes the commercial process used by ICI since 1960 for nitric acid concentration using magnesium nitrate as the mass separating agent. Since 1957, Hercules has operated commercially a similar process using the same separating agent, magnesium nitrate (12). Other industrially important systems that are candidates for separation using salt-effect extractive distillation are discussed by Furter and Cook (1, 2).

Several authors have reviewed the available theories and correlations (1, 2, 13, 14) for mixed-solvent electrolyte systems. Despite their importance, to date no satisfactory theory has been developd for predicting the thermodynamic properties (in particular, activity coefficients and the volumetric equation of state) of mixed-solvent electrolytes. We are currently engaged in the development of a theory for mixed-solvent electrolytes based on a fundamental statistical mechanical approach. The development and validation of such a theory requires experimental phase equilibrium measurements.

As attested to in the review articles by Furter (1, 2), there has been a tremendous amount of experimental data accumulated (particularly in the USSR and Japan) on mixed-solvent electrolyte systems. However, much of these data is at salt saturation only, since this represents the easiest situation experimentally. On the other hand, the development of theories of the salt effect requires vapor–liquid equilibrium data over the whole range of salt concentration (salt free to saturation) in order for there to be a meaningful comparison of theory and experiment. In order to develop a collection of vapor–liquid equilibrium data on mixed-solvent systems spanning the full salt concentration range, experimental measurements have been performed in the Department of Chemical Engineering at the University of Virginia for several years (15–19). The systems studied so far, for which results are described in this paper, are methanol/H_2O/KCl, methanol/H_2O/KBr, methanol/H_2O/NaCl, methanol/H_2O/NaBr, 1-propanol/H_2O/KBr, 1-propanol/H_2O/NaCl, 1-propanol/H_2O/NaBr, and 2-propanol/H_2O/NaBr. The choice of systems is designed to isolate the effect of specific cations and anions (as in the methanol series of experiments) and the contribution of methyl groups in the alcohol. No experiments on ethanol-containing systems are necessary due to the extensive published data on these systems.

Most of the results reported in this paper were obtained with a modified Othmer still (described in section 2.1), which is a continuous-distillation still that recirculates the vapor phase only. Several drawbacks in the use of the Othmer still, and the desirability of checking the results with an independent experimental technique, led to the use of a modified Boublík–Benson still for one system, 2-propanol/H_2O/NaBr. This is a continuous distillation still that recirculates both liquid and vapor phases. As described in section 2.2, the Boublík–Benson still eliminated some of the difficulties of operation of the Othmer still but introduced some new problems as well. All the experiments are performed at ambient pressure.

Section 2 contains the details of the experimental procedures. In section 3, the results obtained from the experimental studies are described. Section 4 contains our conclusions and observations.

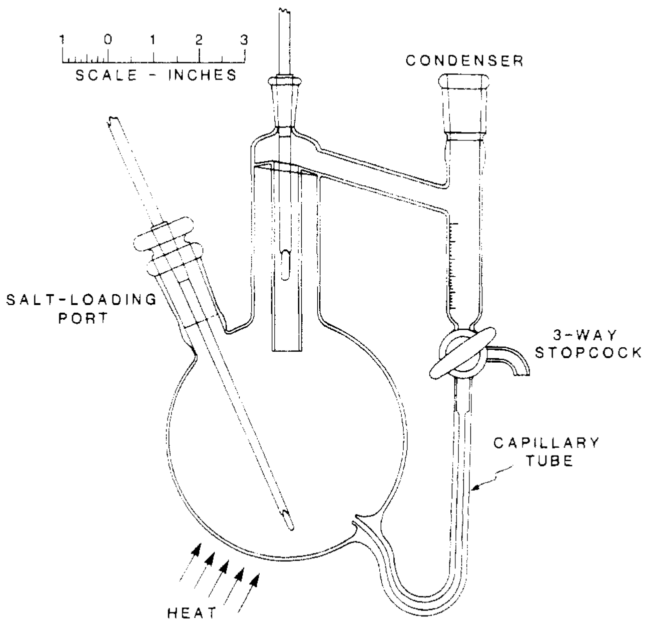

Figure 1. Modified Othmer still.

2. Experimental Procedures

2.1. Othmer Still. 2.1.1. Description of Still. The apparatus chosen for most of the course of this study was Johnson and Furter's modified version (20) of the Othmer recirculation still (21), shown in Figure 1. Because of the ease of operation and design features, the modified Othmer still provides accurate vapor–liquid equilibrium data in a relatively short experimental time.

Although Othmer's original still is noted for its simplicity of design and operation and for giving consistent data, Johnson and Furter (20) found it necessary to modify the still for use in the study of salt solutions. The original recirculation still, as designed by Othmer, had a small drainage port near the bottom of the still pot. During trials of salt-containing solutions, Johnson and Furter found that the port became a trap for undissolved salt particles and prevented thorough mixing of the still's liquid phase. In addition, the port often became clogged with salt when the still's contents were emptied. These problems were eliminated by removing the drainage port and positioning a widened loading port in the side of the pot next to the vapor jacket. This widened port facilitated the addition of salt and cleaning of the still pot. The loading port was further adapted to hold a thermometer for measurement of the solution temperature.

A second modification made by Johnson and Furter to Othmer's original still (21) was the lengthening of the internal vapor jacket. The short jacket featured in Othmer's design minimized the heat loss while preventing reflux from occurring within the still. By lengthening the vapor jacket, the possibility of salt particles being carried over into the condensed vapor chamber was virtually eliminated. Johnson and Furter found, however, that it was necessary to heat the vapor space 2–3 °C above the solution boiling point to prevent refluxing. To accomplish this, the vapor jacket was wrapped with an electrical heating tape controlled by a variable power source.

The third modification to the Othmer still was the replacement of the constant volume condensate chamber with a graduated condensate chamber fitted with a three-way stopcock. This increased the flexibility of the still since the volume of holdup and sample size can be controlled. With the stopcock in a wide open position, all of the condensed vapor is returned to the still pot (zero holdup). By varying the position of the stopcock, the holdup may be maintained at any desired level. When sufficient time had elapsed and the system was thought to have achieved equilibrium, the stopcock was rotated and a measured sample was removed through the sample spout. This procedure enabled the operator to take a sample in a very short time and reduce any sampling error.

To provide proper mixing of the still contents and to maintain a sufficient condensate holdup for recirculation to ensure a rapid approach to steady state (at which point the liquid and vapor condensate compositions are essentially equal to the liquid–vapor equilibrium compositions), vigorous boiling was necessary. As in any boiling solution, droplets formed on the inner surfaces of the container. While a superheated vapor space was required to prevent refluxing, too much superheat caused the droplets on the inner surfaces of the glassware to vaporize, or flash. Such flashing left deposits of salt above the liquid level, thereby changing the salt composition in the pot. Since this situation was highly undesirable, the superheat needed to be maintained carefully. A stream of air passed over the exterior of the still above the liquid level was found to be useful in controlling the proper temperature differential.

The positioning of the stopcock, above the level of the solution, prevented contamination of the condensed vapor sample by back-mixing with the salt-containing solution in the still pot. In addition, the return line connecting the sample chamber and the still pot was constructed with the line dipping below the bottom of the flask. This provided a trap to prevent vapor formed on the bottom of the flask from reaching the condensate chamber. The positioning of the return line in the bottom of the still pot also provided mixing action during still operation.

The still used in the present study was made in the glass shop in the Department of Chemistry at the University of Virginia, based on specifications given by Furter (*20*) and Johnson and Furter (*21*).

2.1.2. Operation of the Modified Othmer Still. The accurate preparation of the initial solution to be charged to the still was extremely important since liquid compositions throughout the experiment are calculated by overall material balance based on that of the initial mixture. In each experimental run, an initial alcohol/water solution of about 700 mL was prepared using volumetric pipettes to ensure accurate compositions. Between 350 and 500 mL of the initial solution was charged to the still. Aliquots of the remaining solution were used to rinse the feed port and still walls after each salt addition.

The variation in the volume of the initial charge to the still was motivated by the observation that solutions high in water content had a capacity to hold large volumes of salt. By varying the initial charge to the still, the situations was avoided where large amounts of salt increased the solution volume to the point of interfering with the proper operation of the still. Back-mixing and contamination of the condensed vapor sample are the possible results of too large a liquid solution volume. Therefore, rather than charging the still with 500 mL in every case, the initial charge of solutions where large amounts of salt were needed to approach saturation is limited to 350 mL. As solubilities decreased, the initial charge was increased, reaching a maximum of 500 mL.

The volume of the initial solution charged to the still was measured by using volumetric pipets and was introduced into the still through the loading port in the side of the still. To provide for superheating the vapor space during still operation, the neck of the still is wrapped with electrical heating tape, which was controlled by a variable power source (Powerstat, manufactured by The Superior Electric Company, Bristol, CT). The heating tape was in turn covered with aluminum foil and then wrapped in several layers of asbestos insulating tape. The asbestos gauze is wrapped to within $^1/_2$ in. of the still's liquid level. The $^1/_2$-in. space between the insulating tape and the liquid level helped to prevent flashing and allowed the observer to determine if salt had crystallized on the inner walls of the still above the liquid level.

The heat source for the experiments was provided by two small bunsen burners. The burners were positioned to supply heat midway between the point where the condensate return line enters the still pot and the liquid level on the far side of the pot from the return line. To avoid the development of hot spots on the still's surface, the bottom of the still was fitted with asbestos-coated wire gauze. These pads were shaped to conform to the shape of the bottom of the still, which provided more even distribution of the heat, prevented boiling of the liquid solution in the return line, and dissipated heat from the external surface of the still away from the vapor space inside the still. Additionally, some boiling stones were added to smooth the boiling action and to minimize splashing of the solution onto the upper surfaces of the still.

Once the solution achieves a steady boil, the variable power source was turned on to control the superheat of the vapor space. The still was operated at zero holdup until a superheat of between 2 and 6 °C is obtained. The stopcock was then closed until the condensate level reached approximately 10 mL. The stopcock was then adjusted to maintain the condensate at this level. Frequent minor adjustments were necessary.

Because the volume of condensate in the sample chamber was very small compared to the volume of solution in the still pot (<3%), equilibrium was approached rapidly. Johnson and Furter (*20*, *21*) reported that, in the time necessary to condense the initial sample volume, the system approached 99% of equilibrium. Therefore, the system was maintained at constant holdup for 10–15 min before any sample was taken. Since the condensate volume represented such a small fraction of the total volume, fluctuations of 1–2 mL were tolerated during the holdup period.

After 10–15 min at constant holdup, the vapor and liquid temperatures were recorded and the sample of the condensate was quickly withdrawn through the sample spout into a sample vial. The samples (approximately 10 mL) were immediately sealed with paraffin and capped and then placed in a constant-temperature bath. The still remained in operation during the brief sampling period. Part of the condensate remained in the condensate chamber in order to prevent vapors from escaping.

After the sample was taken, the burners and power source were turned off. The system was then allowed to cool 20–30 °C below the temperature of the boiling solution to minimize the amount of vapor that would escape through the loading port when the salt was added for the next run. Since escaping vapor could not be accounted for, the composition of the remaining solution would be affected and the experimental accuracy would suffer.

After the contents of the still were cooled, a preweighed amount of dried salt was added through the large loading port. Material balance calculations were performed to predict the amount of salt necessary to change the mole fraction of salt by reasonable increments. The salt was introduced into the still pot by using a funnel with a long, wide spout. The funnel, loading port, and still walls near the port were rinsed with 10-mL aliquots from the initial solution until no visible salt residue remained. A volumetric pipet was used to introduce the rinse aliquots. The weights of the salt and rinse solution were recorded in order to calculate changes in the liquid composition. The composition of the rinse aliquots were the same as the initial still charge.

The operating procedure, beginning at the point where the burners are turned on, was repeated as described previously. The entire process was continued, with further additions of salt, until the solution was saturated. Saturation in this study refers to a solution that contains undissolved salt in the bottom of the still.

2.1.3. Analysis of Samples. The samples were analyzed by a method similar to the Westphal Balance density determination technique. A "bob" was suspended in the condensed vapor sample and weighed to five significant figures with a Mettler H51AR balance, which approximated the Westphal procedure. The composition was calculated from a calibration curve derived from measurements on standard solutions.

The liquid composition was determined by material balance. As noted before, the salt additions and rinse aliquots were recorded in order to keep an accurate account of the liquid composition during the experiments. Later, after the condensate samples were weighed and their compositions determined, the liquid compositions were further corrected for the amount and composition of the condensate in the condensate holdup chamber and the condensate samples themselves. The mass of the vapor in the vapor space of the still was not accounted for, nor was there any attempt to account for vapors escaping through the condensor or through the loading port during the salt additions at 20–30 °C below the boiling point of the solution. In section 3, error estimates are provided for the vapor and liquid compositions in the modified Othmer still experiments. These estimates are based on standard propagation of errors analysis of the material balance equations. The inputs to the estimate are the known inaccuracies in the Mettler balance, the volumetric measurements, and the composition–bouyancy correlation. This analysis does not take into account errors introduced by the unmeasured vapor volume and possible vapor losses described above. The estimated errors in liquid mole fractions range from 0.0001 to 0.005 and in vapor mole fractions from 0.0001 to 0.009. The error estimates should be regarded as lower bounds on the error in each experimental system, with lower error estimates indicating greater precision in the volumetric and mass measurements. A more accurate picture of the actual error in the experimental results is obtained from independent replicate experiments performed by different members of the research group. These indicate that the error in the compositions is at most 0.01 in mole fraction and in most cases is closer to 0.005 in mole fraction.

2.2. Modified Boublǐk–Benson Still. 2.2.1. Description of Still. As noted above, during the operation of the Othmer still vigorous boiling caused salt deposits to form on the interior of the vapor space due to flashing of liquid droplets. These salt deposits were removed, and the salt was reintroduced into the liquid phase, by washing the interior of the still with portions of the original salt-free alcohol/water solution. This prevented the liquid-phase salt concentration from changing by large amounts and allowed the liquid-phase salt concentration to be determined by overall material balance (taking into account the wash solution additions and sample removals). However, it is clear that the addition of the extra alcohol/water solution to the system lowers the overall salt composition (although probably to a lesser degree than would be the case if the salt deposits were not washed back into solution). An alternative solution is to use a still that continuously flushes areas where salt can possibly deposit. A still that circulates both liquid and vapor phases can meet such a requirement; in addition, one can expect to obtain more accurate equilibrium temperatures and compositions from such stills (*23*).

Figure 2 depicts schematically the design of the still used for the present work. This design is very close to that used by Dvorak and Boublǐk (*24*) and Boublǐk and Benson (*25*). These researchers employed this apparatus design in equilibrium measurements of volatile nonelectrolyte systems. No evidence concerning the use of this kind of still being used for electrolyte systems was found during the literature search for this research. The dimensions of the modified Boublǐk–Benson still used in this research are as follows: the Cottrell pump is 38.1 cm in length with an internal diameter of 0.5 cm; the equilibrium and separating cell is 24.1 cm tall and 5.7 cm wide and contains seven coils with an internal diameter of 0.4 cm.

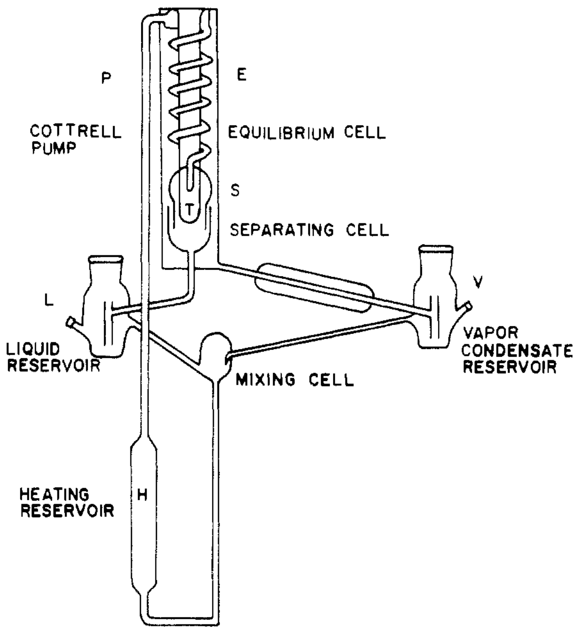

Figure 2. Modified Boublǐk–Benson two-phase recirculation still.

The circulation of the vapor and liquid phases in the still begins in the heating reservoir, H, where the boiling liquid forces liquid and vapor up the Cottrell pump, P. Reservoir H was heated by using thermal tape and a variable powerstat. The interior of the heating reservoir was lined with a ground-glass frit to provide smooth evolution of bubbles. The two phases then flow into the top of the equilibrium cell, E, and then flow down the coils where the mixing of the two phases ensures equilibria between the two phases. After the coil, the flow exits onto the bottom of the temperature finger, T, in the separation cell, S. An inch of oil in the temperature well serves as a medium for the sensor of a digital thermometer measuring tenths of degrees Centigrade. The space around the coil was under a vacuum for insulation purposes. When the system is at steady-state temperature, the vapor flows around the bell glass toward the vapor reservoir, V. The vapor is condensed before reaching the reservoir. The liquid, meanwhile, drips straight down off the finger and flows left to the liquid reservoir, L. Both of these reservoirs were mixed vigorously by water driven magnetic stirrers. The intense mixing was necessary for homogeneity in the collection reservoirs; otherwise density gradients due to temperature or composition can create layers of differing composition in the reservoirs. The water driving the stirrers was also used for cooling medium in the condensers. The overflow from these reservoirs flows into a remixing chamber before reentering the heating reservoir.

The still consisted of six pieces and was custom built by the glass blower in the Department of Chemistry at the University of Virginia. The modular construction facilitated repair and cleaning.

2.2.2. Operation of the Modified Boulbǐk–Benson Still. The still operated with a solution charge of 70–72 mL. Fifty milliliters of charge solution were poured into the heating reservoir. The remaining charge, 20–22 mL, was poured into the liquid reservoir. There was no liquid placed in the vapor side since any solution in that reservoir not of the equilibrium vapor composition must be thoroughly flushed out of the reservoir. The liquid, remixing, and heating reservoirs were big enough to hold the 70–72 mL of charge. An inch of pump oil was poured into the temperature well and the digital thermometer sensor inserted into it. The thermal taped portions of the still and the top of the equilibrium cell were also wrapped with aluminum foil for insulating purposes. With proper heating, the first drop of condensate comes off in the vapor reservoir after about 15 min, and the reservoir was usually filled after roughly 30 or 35 min. At steady-state temperature, the drip rate from the drop counter in the remixing reservoir was about 30 drops/min. This rate allowed the reservoir to be flushed several times by the time the still had been running for an hour.

The still reached equilibrium after an hour of operation. After the system reaches equilibrium, the operating temperature is recorded. The temperature is measured with a platinum resistance thermal conductivity probe connected to a digital thermometer manufactured for Fisher Scientific. This thermometer measures temperature to the nearest 0.1 ± 0.2 °C and comes with a digital calibrator. Its accuracy was also compared with an NBS traceable mercury thermometer, and it was found to be within the 0.2 °C claimed by the manufacturers. The ambient air pressure is also recorded from a barometer. As a check on both the still operation and the accuracy of the barometer, the still was run with distilled, deionized water to obtain the boiling point of water. It was found that there was less than a 0.5% difference between the pressure readings from the barometer and the calculated pressure from literature values for the saturated vapor pressure of water.

Since the still was operated at ambient pressures, the sampling was done through the top of the ground standard taper joints for the condensers. The condenser was lifted out of the joint, and a 3-5-mL sample is quickly withdrawn with a Pasteur pipet. The sample was placed in a 7-mL screwcap vial with a Teflon-lined silicone septum for gas chromatograph and ion concentration analysis. This vial was airtight when sealed, and samples were withdrawn from the vessel with a syringe. Ionic activity sample preparation from these vials was a little different, and both of these procedures are described in more depth later in this section.

2.2.3. Analysis of Samples. The modified Othmer still was used for obtaining vapor-liquid equilibrium measurements on all the alcohol/water/salt described in the Introduction. To date, the Boublík-Benson still has been used only for the 2-propanol/H_2O/NaBr system. The use of a completely independent method for obtaining vapor-liquid equilibrium data is useful for validating the modified Othmer still results. In future publications, further results obtained with the modified Boublík-Benson still will be reported.

The charge solutions for the Boublík-Benson still were prepared from distilled, deionized water and Baker Analyzed isopropyl alcohol. Four salt-free mole fractions of 2-propanol in water were charged to the still, x_{PrOH} = 0.300, 0.500, 0.700, and 0.800. From 2 L of initial solution, aliquots of 150 g were drawn for the actual still charges; from this, one can get two runs out the aliquot. The first 150 g of each stock was run salt free in the still, and into each of the subsequent 150-g portions were dissolved increasing amounts of salt.

Most of the composition analysis was performed by a Hewlett-Packard Model 5800A gas chromatograph by using thermal conductivity detection. The column was a 4-ft glass column packed with a polar separating polymer packing, Poropak T. Since the liquid side samples contained salt, crystallized salt built up on the front end of the glass column. The caked salt changed the characteristics of the column, so after the salt built up significantly from repeated sample injection, the column was removed and the first inch of column packing was replaced. After replacing the packing, the column needed to stabilize for 24 h. The gas chromatograph was calibrated by measuring responses for a set of nine prepared samples of 2-propanol/water solutions ranging in mole fraction from 0.150 to 0.950. The calibration curve was fitted to cubic splines to permit rapid calculation of compositions from peak areas.

For some of the samples with low mole fractions of 2-propanol, the composition reproducibility was poor on the gas chromatograph because the low end of the calibration curve was not very reproducible. These samples were best analyzed by a standard addition method. A precisely weighed amount of sample was transferred into a septum vial, and a known amount of 2-propanol was added to the sample. This method brought the GC chromatogram into the center region of the calibration curve where the reproducibility was best. The computation of the composition of liquid side samples took into account the salt concentration determined from ionic activity, the salt-free gas chromatograph assay, and the mass of the sample. [Since the salt did not appear in the vapor phase, the composition of the vapor condensate samples was determined straightforwardly solely by the gas chromatographic analysis.] The concentration of the Na^+ ion in parts per million was measured by a Pope Model 1500 pH/ion meter. The analysis was calibrated with four or five standards prepared from a standard traceable to NBS Standard Reference Material. Periodic checks on the calibration curve revealed that the slope did not change over the course of the experiments with the modified Boublík-Benson still.

Accurate ion analysis also required a dilution procedure. A small aliquot from a liquid side sample of the still was placed in a preweighed volumetric flask and then reweighed for the sample mass. It was then diluted with distilled, deionized water in a controlled fashion to ensure complete dissociation of the salt in solution and to eliminate interference from the organic in the sample. The sample was reweighed after dilution to determine the dilution ratio. Each sample was analyzed three times, and the readings were averaged to determine the salt composition.

3. Results

In this section, the vapor-liquid equilibrium results obtained during the course of this study are presented. For each system, the results were checked for consistency with published salt-free and saturated salt vapor-liquid equilibrium data. The usual check for thermodynamic consistency of vapor-liquid equilibrium data, the Gibbs-Duhem relation, could not be used in the present study due to the absence of salt in detectable quantities in the vapor phase. The relative volatility of alcohol (A) to water (W)

$$\alpha_{\mathrm{A/W}} = \frac{y_{\mathrm{A}} x_{\mathrm{W}}}{y_{\mathrm{W}} x_{\mathrm{A}}} \tag{2}$$

obtained in the experiments is also reported.

In some of the earlier studies (*15*, *16*) performed at the University of Virginia, the boiling point temperatures of some of the alcohol/water/salt mixtures were not recorded. This is evident in Tables I-IV, where, for each experimental run (in which the ratio of alcohol to water is held approximately constant as the salt concentration is varied from zero to saturation), only the temperature range is reported. In later studies (*17*-*19*), the boiling point temperatures were recorded. This permitted the calculation of the water and alcohol activity coefficients, γ_{A} and γ_{W}, respectively, from the usual relation for liquid-vapor equilibrium at low pressures (*26*):

$$y_i \phi_i P = x_i \gamma_i \phi_i^{\mathrm{s}} P_i^{\mathrm{s}} \tag{3}$$

In this equation, y_i and x_i are the mole fractions of component i in the vapor and liquid phase, respectively, $\phi_i = \phi_i(T,P,\vec{y})$ is the fugacity coefficient of component i in the vapor mixture phase, $\phi_i^{\mathrm{s}} = \phi_i^{\mathrm{s}}(T)$ is the fugacity coefficient of pure vapor i in the saturated vapor state at temperature T, $P_i^{\mathrm{s}} = P_i^{\mathrm{s}}(T)$ is the

Table I. Selected Experimental Results for the Methanol/Water/KCl System (*15*)

T, °C	x_{salt}	x_A	y_A	$\alpha_{A/W}$
93.0–96.0	0.000	0.072	0.353	7.03
	0.013	0.070	0.367	7.60
	0.038	0.066	0.399	9.01
	0.050	0.064	0.411	9.66
	0.074	0.059	0.432	11.18
	0.086	0.057	0.447	12.15
84.0–86.0	0.000	0.148	0.539	6.73
	0.011	0.146	0.564	7.47
	0.022	0.143	0.581	8.10
	0.033	0.140	0.600	8.86
	0.044	0.138	0.618	9.59
	0.055	0.135	0.630	10.22
	0.065	0.132	0.643	10.96
81.5–83.5	0.000	0.195	0.589	5.92
	0.011	0.192	0.615	6.63
	0.022	0.190	0.641	7.40
	0.033	0.187	0.655	7.92
	0.044	0.184	0.674	8.67
	0.055	0.180	0.690	9.46
79.0–81.0	0.000	0.257	0.657	5.54
	0.013	0.255	0.682	6.16
	0.026	0.252	0.707	6.91
	0.039	0.249	0.724	7.50
	0.052	0.247	0.737	7.95
75.5–77.5	0.000	0.384	0.754	4.92
	0.008	0.381	0.759	5.05
	0.016	0.379	0.765	5.20
	0.029	0.376	0.771	5.33
72.5–74.5	0.000	0.576	0.822	3.40
	0.008	0.579	0.828	3.54
	0.011	0.570	0.831	3.62
	0.014	0.568	0.834	3.70
68.5–70.5	0.000	0.788	0.914	2.86
	0.002	0.787	0.917	2.96
	0.004	0.786	0.917	2.95
	0.006	0.785	0.917	2.94

Table II. Selected Experimental Results for the Methanol/Water/NaCl System (*15*)

T, °C	x_{salt}	x_A	y_A	$\alpha_{A/W}$
88.0–90.0	0.000	0.107	0.450	6.83
	0.029	0.102	0.509	8.75
	0.043	0.100	0.527	9.55
	0.058	0.097	0.552	10.75
	0.071	0.095	0.567	11.50
84.5–86.5	0.000	0.150	0.534	6.49
	0.014	0.147	0.562	7.32
	0.028	0.144	0.588	8.21
	0.041	0.141	0.604	8.85
	0.067	0.136	0.644	10.60
82.0–84.0	0.000	0.197	0.595	5.99
	0.030	0.191	0.646	7.44
	0.045	0.189	0.678	8.53
	0.059	0.186	0.696	9.29
79.5–81.5	0.000	0.249	0.646	5.50
	0.013	0.246	0.671	6.14
	0.026	0.243	0.689	6.67
	0.039	0.241	0.713	7.42
	0.052	0.237	0.728	8.03
78.0–80.0	0.000	0.307	0.688	4.98
	0.015	0.304	0.714	5.59
	0.030	0.302	0.737	6.20
	0.045	0.299	0.754	6.73
75.5–77.5	0.000	0.406	0.756	4.53
	0.023	0.401	0.787	5.31
	0.034	0.398	0.797	5.60
72.5–74.5	0.000	0.571	0.828	3.62
	0.008	0.569	0.834	3.74
	0.015	0.567	0.841	3.90
	0.023	0.565	0.847	4.04
68.5–70.6	0.000	0.775	0.902	2.67
	0.009	0.773	0.909	2.82
	0.013	0.772	0.911	2.85

Table III. Selected Experimental Results for the KBr/Methanol/Water System (*16*)

T, °C	x_{salt}	x_A	y_A	$\alpha_{A/W}$
90.0–94.0	0.000	0.092	0.431	7.48
	0.023	0.083	0.453	8.92
	0.044	0.075	0.463	10.14
	0.064	0.066	0.466	11.50
	0.092	0.058	0.485	13.80
	0.127	0.048	0.507	17.68
81.0–82.0	0.000	0.220	0.628	5.99
	0.026	0.205	0.660	7.28
	0.050	0.192	0.689	8.75
	0.072	0.179	0.704	9.95
	0.105	0.164	0.718	11.35
76.0–77.0	0.000	0.391	0.754	4.77
	0.008	0.380	0.761	5.13
	0.016	0.370	0.763	5.34
	0.027	0.358	0.771	5.78
	0.037	0.347	0.775	6.12
	0.083	0.316	0.789	7.11
74.0–75.0	0.000	0.502	0.781	3.54
	0.008	0.491	0.799	4.04
	0.021	0.479	0.802	4.24
	0.033	0.466	0.820	4.90
	0.044	0.453	0.827	5.31
	0.074	0.432	0.823	5.32
70.5–71.0	0.000	0.707	0.877	2.96
	0.005	0.698	0.878	3.06
	0.010	0.690	0.879	3.16
	0.016	0.682	0.881	3.28
	0.034	0.665	0.885	3.48

saturated vapor pressure of pure i, and $\gamma_i = \gamma_i(T,P,\vec{x})$ is the activity coefficient of component i in the liquid phase. The only approximation in eq 3 is the neglect of the Poynting correction, which is negligible at the low pressure (1 atm) of the present experimental study. Equation 3 can be rearranged to give

$$\gamma_i = \frac{y_i \phi_i P}{x_i \phi_i^s P_i^s} \qquad (4)$$

In order to calculate γ_i from experimental T-x-y measurements, the fugacity coefficient ϕ_i must be estimated. In this work, ϕ_i is approximated by the virial equation truncated at the second virial coefficient

$$\phi_i(T,P,\vec{y}) = \exp\left[\left(2\sum_{j=1}^{N_c} y_j B_{ij} - B\right)\frac{P}{RT}\right] \qquad (5)$$

Table IV. Selected Experimental Results for the NaBr/Methanol/Water System (*16*)

T, °C	x_{salt}	x_A	y_A	$\alpha_{A/W}$	T, °C	x_{salt}	x_A	y_A	$\alpha_{A/W}$
88.9–100.0	0.000	0.096	0.454	7.84	77.0–81.0	0.000	0.389	0.711	3.86
	0.033	0.085	0.465	9.02		0.022	0.373	0.740	4.62
	0.062	0.076	0.500	11.34		0.043	0.357	0.755	5.18
	0.095	0.066	0.527	14.16		0.072	0.339	0.776	6.03
	0.164	0.049	0.545	19.24		0.090	0.324	0.786	6.64
83.0–89.5	0.000	0.191	0.593	6.17		0.124	0.305	0.809	7.93
	0.056	0.164	0.635	8.27	74.0–77.0	0.000	0.510	0.785	3.64
	0.092	0.151	0.671	10.23		0.033	0.477	0.813	4.47
	0.126	0.137	0.685	11.70		0.064	0.456	0.835	5.34
	0.166	0.123	0.710	14.13		0.118	0.416	0.869	7.43
79.5–83.5	0.000	0.300	0.667	4.67	70.0–73.0	0.000	0.711	0.878	2.93
	0.024	0.284	0.691	5.45		0.011	0.698	0.888	3.31
	0.047	0.270	0.716	6.38		0.028	0.682	0.893	3.55
	0.075	0.255	0.739	7.44		0.054	0.659	0.902	4.01
	0.107	0.237	0.760	8.75		0.092	0.627	0.911	4.57
	0.148	0.218	0.785	10.60					

where R is the gas constant and B, the second virial coefficient, is given by

$$B = \sum_{i=1}^{N_0} \sum_{j=1}^{N_0} y_i y_j B_{ij}(T) \qquad (6)$$

In this equation, $B_{ij}(T)$ is the second virial coefficient characterizing interactions between species i and j molecules and N_0 is the number of species present in the vapor phase. The pure-component (B_{ii}) and cross (B_{ij}) second virial coefficients were calculated from the correlation of Hayden and O'Connell (*27*). For pure components, the correlation requires the critical temperature and pressure, Thompson's mean radius of gyration, the dipole moment, and, if necessary, a chemical association parameter. For cross coefficients, mixing rules are used and solvation effects are accounted for in a manner similar to association effects. Equation 5 was used to calculate both ϕ_i and ϕ_i^s in eq 4. The saturated vapor pressures of pure alcohol and pure water were calculated from the Antoine equation.

As might be expected, but cannot be ruled out a priori, the fugacity coefficients calculated by the Hayden–O'Connell correlation at the operating conditions of the experiments reported in this paper were near unity. Certainly, the uncertainty introduced into the values of γ_i by the neglect of the ϕ_i and ϕ_i^s are much smaller than the uncertainties in the measured T–x–y data.

3.1. Results for Methanol/H_2O with KCl and NaCl. Vapor–liquid equilibrium measurements for these systems measured with use of the modified Othmer still (*15*) are reported in Tables I and II. Analysis of the error accumulation in the experimental procedure yielded the following estimates of errors in composition due to measurement limitations $\delta y_i = \pm 0.009$ and $\delta x_i = \pm 0.003$ (i = A, W) and $\delta x_{salt} = \pm 0.0001$. In computing errors, uncertainties in liquid densities, liquid volumes, weighing operations, and curve calibrations were taken into account. (Note, however, the discussion regarding error estimates in section 2.1.3.)

Johnson and Furter (*28*) have reported vapor–liquid equilibrium data for methanol and water in the absence of salt and for solutions saturated with KCl and with NaCl at atmospheric pressure. The salt-free and salt-saturated systems in the present study (the largest salt concentration reported at each set of approximately constant x_A/x_W experiments) agreed very well with Johnson and Furter's data. This comparison can be made quantitatively as follows: on a y–x plot, a smooth curve is drawn through the results given in Tables I and III. For the liquid compositions x_i given by Johnson and Furter, the value obtained from the smoothed curve for the corresponding vapor composition y_i is compared with the value reported by Johnson and Furter. For salt-free methanol/water, the average deviation between the results reported here and those of Johnson and Furter is less than 0.01 in mole fraction. The average deviations are less than 0.005 and 0.006 in mole fraction for methanol/water saturated with KCl and NaCl, respectively.

Table V. Selected Experimental Results for the KBr/1-Propanol/Water System (*17*)

T, °C	x_{salt}	x_A	y_A	γ_A	γ_W	$\alpha_{A/W}$
87.8	0.000	0.100	0.371	5.44	1.17	5.31
87.9	0.019	0.095	0.378	5.83	1.11	5.71
87.5	0.037	0.086	0.401	6.86	1.09	6.79
87.0	0.055	0.079	0.422	8.11	1.09	8.07
87.5	0.073	0.071	0.456	9.50	1.02	10.11
87.9	0.096	0.063	0.477	11.04	0.98	12.19
88.2	0.114	0.055	0.497	12.91	0.94	14.81
89.5	0.134	0.049	0.506	14.25	0.90	17.25
90.0	0.153	0.041	0.510			20.32
87.0	0.000	0.202	0.389	2.90	1.25	2.52
87.9	0.028	0.190	0.452	3.47	1.10	3.40
88.0	0.052	0.178	0.484	3.95	1.05	4.07
88.2	0.080	0.165	0.521	4.56	0.99	5.00
88.8	0.102	0.153	0.561	5.16	0.90	6.23
89.0	0.123	0.146	0.590			7.20
86.8	0.000	0.306	0.395	1.97	1.43	1.49
87.0	0.026	0.296	0.455	2.32	1.31	1.92
87.4	0.047	0.284	0.490	2.56	1.22	2.27
87.8	0.067	0.273	0.661	2.79	1.15	2.63
88.1	0.085	0.261	0.559	3.09	1.06	3.16
88.8	0.101	0.252	0.590			3.71
87.0	0.000	0.407	0.421	1.56	1.59	1.06
87.9	0.024	0.396	0.466	1.72	1.45	1.28
88.1	0.042	0.386	0.509	1.91	1.34	1.54
88.5	0.061	0.374	0.556	2.11	1.21	1.89
89.0	0.077	0.363	0.592			2.24
87.3	0.000	0.509	0.451	1.32	1.80	0.79
87.8	0.011	0.504	0.482	1.40	1.69	0.90
88.1	0.022	0.498	0.516	1.50	1.58	1.03
88.7	0.034	0.491	0.549	1.58	1.45	1.18
89.1	0.044	0.483	0.592			1.42
87.5	0.000	0.612	0.489	1.18	2.11	0.61
87.8	0.007	0.610	0.518	1.24	1.99	0.68
88.2	0.011	0.611	0.543	1.28	1.88	0.74
89.0	0.016	0.608	0.581	1.33	1.69	0.86
89.3	0.021	0.605	0.594			0.90

3.2. Results for Methanol/H_2O with KBr and NaBr. Vapor–liquid equilibrium measurements for methanol and water with varying concentrations of KBr and NaBr measured with use of the modified Othmer still (*16*) are reported in Tables III and IV. For these measurements, Baker (*16*) estimated that the errors in the vapor and liquid mole fractions were $\delta y_i = \pm 0.005$ and $\delta x_i = \pm 0.005$.

The authors could not find any published data on methanol/water saturated with KBr and with NaBr. Consequently, one

Table VI. Selected Experimental Results for the NaCl/1-Propanol/Water System (*17*)

T, °C	x_{salt}	x_A	y_A	γ_A	γ_W	$\alpha_{A/W}$
87.9	0.000	0.101	0.372	5.39	1.10	5.29
86.5	0.020	0.096	0.408	6.56	1.11	6.37
86.3	0.038	0.089	0.439	7.65	1.08	7.68
86.5	0.055	0.083	0.461	8.55	1.04	8.88
87.2	0.071	0.077	0.484	9.37	0.98	10.35
88.2	0.085	0.072	0.498	9.90	0.90	11.55
88.5	0.102	0.067	0.515			13.23
87.0	0.000	0.203	0.390	2.90	1.25	2.52
87.1	0.026	0.193	0.439	3.42	1.17	3.18
87.9	0.049	0.183	0.481	3.82	1.07	3.88
88.3	0.071	0.176	0.518			4.59
87.2	0.000	0.306	0.396	1.94	1.41	1.49
87.2	0.012	0.301	0.426	2.14	1.36	1.70
87.0	0.023	0.294	0.446	2.29	1.32	1.87
87.5	0.035	0.285	0.472	2.44	1.24	2.13
88.0	0.048	0.277	0.488	2.55	1.19	2.32
88.0	0.058	0.272	0.505	2.69	1.16	2.51
88.2	0.066	0.265	0.514			2.66
87.0	0.000	0.407	0.421	1.56	1.59	1.06
87.8	0.014	0.399	0.461	1.69	1.45	1.26
88.2	0.027	0.392	0.486	1.78	1.38	1.40
88.5	0.037	0.386	0.510	1.88	1.31	1.56
88.6	0.046	0.380	0.520			1.63
87.4	0.000	0.508	0.451	1.32	1.79	0.80
87.0	0.002	0.508	0.465	1.35	1.75	0.84
87.5	0.003	0.508	0.470	1.37	1.74	0.85
87.3	0.005	0.508	0.485	1.42	1.71	0.90
87.8	0.007	0.508	0.490	1.41	1.66	0.92
87.8	0.009	0.507	0.504	1.45	1.62	0.97
88.0	0.011	0.507	0.507	1.45	1.60	0.98
88.2	0.013	0.505	0.521			1.04
87.1	0.000	0.305	0.396	1.95	1.41	1.49
87.8	0.028	0.295	0.473	2.34	1.23	2.06
88.1	0.044	0.285	0.507	2.57	1.15	2.42
88.8	0.067	0.272	0.553	2.86	1.03	3.00
90.0	0.089	0.260	0.594	3.06	0.91	3.66
90.3	0.106	0.249	0.626	3.33	0.84	4.33
91.2	0.122	0.238	0.652			5.05
87.0	0.000	0.407	0.421	1.56	1.59	1.06
87.8	0.026	0.395	0.480	1.78	1.42	1.35
88.2	0.050	0.382	0.538	2.01	1.28	1.71
89.2	0.074	0.368	0.585	2.20	1.12	2.14
90.5	0.094	0.354	0.644			2.82

Table VII. Selected Experimental Results for the NaBr/1-Propanol/Water System (*17*)

T, °C	x_{salt}	x_A	y_A	γ_A	γ_W	$\alpha_{A/W}$
87.4	0.000	0.100	0.371	5.52	1.12	5.31
87.6	0.014	0.095	0.412	6.40	1.05	6.57
87.7	0.028	0.088	0.438	7.38	1.01	7.88
88.0	0.040	0.081	0.467	8.36	0.95	9.52
88.1	0.056	0.074	0.492	9.60	0.91	11.39
88.3	0.070	0.067	0.520	11.12	0.86	14.02
88.4	0.081	0.060	0.541	12.87	0.83	16.78
88.9	0.091	0.054	0.552	14.30	0.80	19.56
89.1	0.102	0.047	0.568	16.78	0.77	23.82
90.0	0.114	0.041	0.571	18.67	0.74	27.54
92.0	0.126	0.035	0.583	20.67	0.67	33.94
95.1	0.147	0.028	0.590			42.33
86.9	0.000	0.212	0.490	2.92	1.25	2.53
87.0	0.022	0.194	0.439	3.41	1.17	3.15
87.8	0.046	0.183	0.486	3.88	1.05	3.98
88.5	0.070	0.172	0.532	4.40	0.95	4.99
89.0	0.092	0.163	0.571	4.91	0.87	6.10
90.8	0.117	0.152	0.615	5.26	0.75	7.67
92.5	0.138	0.142	0.655			9.61
87.2	0.000	0.508	0.451	1.33	1.80	0.80
88.0	0.022	0.497	0.513	1.50	1.59	1.02
89.5	0.043	0.485	0.565	1.59	1.37	1.26
90.2	0.064	0.472	0.611	1.72	1.21	1.54
90.8	0.082	0.459	0.651			1.87
87.5	0.000	0.612	0.489	1.18	2.11	0.61
88.0	0.009	0.609	0.516	1.23	1.98	0.67
88.8	0.017	0.607	0.542	1.25	1.86	0.73
89.2	0.025	0.604	0.566	1.30	1.76	0.80
90.1	0.034	0.599	0.612	1.36	1.54	0.97
91.0	0.042	0.592	0.657			1.18

can compare only the salt-free measurements of the present study with prior published data. As noted above, the salt-free measurements agree very well with Johnson and Furter's salt-free data on methanol/water (*28*).

3.3. Results for 1-Propanol/H_2O with KBr, NaCl, and NaBr. Vapor-liquid equilibrium measurements for 1-propanol and water with varying concentrations of KBr, NaCl, and NaBr obtained with use of the modified Othmer still (*17*) are reported in Tables V-VII. By analyzing the error accumulation in the experimental procedure, Newman (*17*) estimated that the uncertainties in the experimental measurements are δy_i = ±0.0001 and δx_i = ±0.002 (i = A, W) and δx_{salt} = ±0.0001.

The salt-free vapor-liquid equilibrium measurements for 1-propanol and water presented here have been compared to the data of Chu (*29*) and Murti and Van Winkle (*30*). The agreement is excellent with an average deviation of less than 0.005 in mole fraction. Johnson and Furter (*22*) report vapor-liquid equilibrium data for 1-propanol/water saturated with NaCl and KBr; again, the agreement between the saturated-system data and the saturated-salt measurements reported in this section is excellent, with average deviations of less than 0.005 in mole fraction for both salts.

It should be noted that for all three salts at saturation the liquid phase separates into two immiscible liquid phases. Measurements of the liquid-liquid equilibrium were not performed so that the liquid compositions reported in Tables V-VII represent overall liquid compositions. These overall compositions are not sufficient for computing the activity coefficients of the water and the alcohol. Consequently no activity coefficients are reported at saturation.

3.4. Results for 2-Propanol/H_2O with NaBr. Vapor-liquid equilibrium measurements for 2-propanol/water/NaBr obtained with use of the modified Othmer still (*18*) are reported in Table VIII. Measurements obtained with use of the modified Boublik-Benson still are given in Table IX. Walter (*18*) estimates that the uncertainties in the experimental measurements in Table VIII are δy_i = ±0.003 and δx_i = ±0.003. A similar propagation of errors analysis suggests that the errors in the measurements obtained with use of the modified Boublik-Benson still are $\delta y_i = \delta x_i$ = ±0.5%, δx_s = ±1%.

The salt-free vapor-liquid equilibrium measurements for 2-propanol and water presented here have been compared to the data of Chu (*29*), and the agreement is very good, with an average deviation of less than 0.008 in mole fraction. Similar agreement is found between the results reported here and the data of Sada et al. (*31*) for 2-propanol/water saturated with NaBr. Moreover, the modified Othmer still results and the modified Boublik-Benson still results are consistent both for salt-free conditions and with salt added.

As with 1-propanol/water, at saturation with NaBr 2-propanol/water exhibits liquid-liquid immiscibility over a limited range of liquid compositions. However, the vapor-liquid equilibrium compositions reported in Table IX refer to subsaturated conditions at which liquid-liquid immiscibility was not observed.

4. Conclusions

Isobaric vapor-liquid equilibrium (T-x-y) measurements on eight mixed-solvent electrolyte (alcohol/water/salt) systems have been performed. The experimental results over wide ranges of salt concentration for each water/alcohol mixture, thus providing a valuable addition to the published literature on these systems. The choice of the specific systems is particu-

Table VIII. Selected Experimental Results for the NaBr/2-Propanol/Water System (*18*)

T, K	x_{salt}	x_A	y_A	γ_A	γ_W	$\alpha_{A/W}$
357.5	0.000	0.081	0.919	5.79	0.98	11.30
357.2	0.010	0.075	0.525	6.65	0.95	13.48
357.2	0.020	0.069	0.541	7.44	0.92	15.56
357.7	0.030	0.064	0.546	7.95	0.90	17.02
357.2	0.040	0.059	0.569	9.16	0.87	20.16
355.7	0.071	0.048	0.620	13.00	0.83	29.95
355.1	0.090	0.042	0.663	16.27	0.77	40.66
355.7	0.110	0.037	0.697	18.97	0.69	53.03
356.2	0.130	0.032	0.720	22.22	0.63	67.34
358.0	0.150	0.027	0.751			91.93
355.5	0.000	0.184	0.538	2.97	1.10	5.16
354.9	0.010	0.175	0.568	3.37	1.06	6.12
354.9	0.020	0.166	0.578	3.62	1.03	6.72
355.2	0.030	0.158	0.602	3.91	0.96	7.77
354.9	0.040	0.150	0.616	4.26	0.94	8.66
354.2	0.050	0.141	0.638	4.83	0.92	10.11
354.0	0.070	0.132	0.669	5.45	0.85	12.22
354.4	0.090	0.123	0.703	6.06	0.77	15.14
354.9	0.111	0.121	0.738	6.34	0.68	17.88
357.0	0.130	0.112	0.762			21.67
354.7	0.000	0.315	0.574	1.91	1.25	2.93
354.7	0.010	0.306	0.609	2.08	1.15	3.48
354.9	0.020	0.298	0.627	2.19	1.09	3.85
354.5	0.030	0.289	0.647	2.36	1.05	4.32
354.3	0.040	0.280	0.655	2.49	1.03	4.61
354.0	0.049	0.272	0.679	2.69	0.97	5.28
353.5	0.069	0.260	0.708	2.99	0.92	6.25
355.3	0.089	0.249	0.730	3.00	0.80	7.19
355.8	0.129	0.236	0.776			9.47
354.4	0.000	0.410	0.585	1.51	1.43	2.03
354.2	0.010	0.402	0.609	1.62	1.36	2.28
353.9	0.020	0.393	0.625	1.72	1.32	2.49
353.9	0.030	0.384	0.645	1.81	1.25	2.77
354.0	0.040	0.376	0.660	1.89	1.20	3.02
354.0	0.050	0.367	0.675	1.98	1.15	3.30
355.2	0.090	0.341	0.732	2.20	0.93	4.56
355.4	0.110	0.328	0.763			5.52
354.1	0.000	0.540	0.608	1.21	1.75	1.32
354.1	0.010	0.532	0.634	1.28	1.64	1.49
354.0	0.020	0.524	0.659	1.35	1.54	1.68
353.7	0.030	0.516	0.678	1.43	1.48	1.85
354.1	0.040	0.507	0.694	1.47	1.39	2.03
354.9	0.070	0.485	0.738	1.58	1.17	2.58
354.2	0.090	0.470	0.755			2.88
353.7	0.000	0.622	0.664	1.16	1.85	1.20
353.7	0.010	0.614	0.686	1.22	1.74	1.34
353.9	0.020	0.606	0.709	1.26	1.61	1.50
354.1	0.030	0.598	0.729	1.31	1.49	1.67
354.0	0.039	0.590	0.740	1.35	1.44	1.79
354.2	0.050	0.581	0.764			2.06
353.2	0.000	0.722	0.721	1.11	2.13	0.99
354.0	0.020	0.706	0.773	1.18	1.71	1.32
354.0	0.030	0.697	0.795			1.52

Table IX. Selected Experimental Results for the NaBr/2-Propanol/Water System (*19*)

T, K	x_{salt}	x_A	y_A	γ_A	γ_W	$\alpha_{A/W}$
354.8	0.000	0.273	0.549	2.072	1.242	3.240
354.4	0.015	0.265	0.581	2.290	1.178	3.773
354.2	0.031	0.253	0.613	2.553	1.102	4.493
353.8	0.000	0.497	0.609	1.301	1.631	1.547
353.5	0.013	0.474	0.641	1.462	1.471	1.927
353.3	0.020	0.467	0.666	1.544	1.368	2.187
353.1	0.000	0.698	0.696	1.097	2.142	0.992
353.4	0.016	0.686	0.728	1.155	1.913	1.169
353.6	0.032	0.674	0.749	1.200	1.774	1.309
353.6	0.000	0.808	0.779	1.040	2.401	0.838
353.5	0.006	0.802	0.788	1.064	2.315	0.890
353.5	0.010	0.797	0.796	1.082	2.207	0.949

larly useful from the point of view of developing mathematical models and correlations for mixed-solvent electrolytes. Two experimental apparatuses were employed and gave consistent results.

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List of Symbols

B	second virial coefficient
B_{ij}	second virial coefficient characterizing interaction between species *i* and *j* molecules in a mixture
N_o	number of species in the vapor phase
P	pressure
P_i^s	saturated vapor pressure of pure species *i*
R	universal gas constant
T	absolute temperature, K
x_i	mole fraction of species *i* in the liquid phase
$\vec{x}$	vector of mole fractions in the liquid phase
y_i	mole fraction of species *i* in the vapor phase
$\vec{y}$	vector of mole fractions in the vapor phase
Δx_i	error in measured value of x_i
Δy_i	error in measured value of y_i
γ_i	activity coefficient of species *i* in the liquid phase
ϕ_i	fugacity coefficient of species *i* in the vapor phase
ϕ_i^s	fugacity coefficient of pure species *i* in the vapor phase at saturation

Registry No. NaCl, 7647-14-5; NaBr, 7647-15-6; KCl, 7447-40-7; KBr, 7758-02-3; methanol, 67-56-1; 1-propanol, 71-23-8; 2-propanol, 67-63-0.

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Dissociation Constants of Primary Phosphate Ion for pH Control in 20 and 50 Mass % 1-Propanol/Water Solvents from 37 to −10 °C

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Earlier work leading to the standard potential of the Ag/AgCl electrode in 20 and 50 mass % 1-propanol/water solvents at temperatures ranging from 37 to −10 °C has been extended to study the dissociation constants of the primary phosphate ion ($H_2PO_4^-$) in the same media at this temperature range. Cells without liquid junction, Pt;H_2(g, 1 atm)|KH_2PO_4, Na_2HPO_4, NaCl|AgCl;Ag, were used to determine the dissociation constants of $H_2PO_4^-$ in these 1-propanol/water media. Buffer solutions composed of KH_2PO_4 and Na_2HPO_4 were prepared in the molality scale (*m*) and are recommended as standards for pH measurements.

Introduction

The standard potential for the Ag/AgCl electrode in 20 and 50 mass % 1-propanol/water solvents from a wide range of temperatures has been used to study phosphate buffer solutions in the same media at temperatures ranging from 37 to −10 °C. Cells without liquid junction

$$\mathrm{Pt;H_2(g,\ 1\ atm)|KH_2PO_4,Na_2HPO_4,NaCl|AgCl;Ag}$$

were used to determine the dissociation constants of $H_2PO_4^-$ (second acid dissociation constants of H_3PO_4) in 20 and 50 mass % 1-propanol/water media. Over the same temperature range, the thermodynamic quantities for the dissociation process can be derived easily.

The standard potential for the Ag/AgCl electrode in 1-propanol/water solvents has been determined by several authors (*1*-*4*). The values used in this investigation were those of Elsemonghy and Fonda (*4*). Some of the needed values were extrapolated or interpolated when necessary. The E_m values used are tabulated in Table I. The measurements were made (± 0.05 mV) with a Fluke Model 8000A potentiometer. The temperature measurements were made in a thermostated bath to ±0.05 °C precision. We have now investigated the second dissociation of H_3PO_4 in 20 and 50 mass % below 0 °C. These solutions are useful as reference standards for pH measurements and control in processes such as the separation of blood plasma protein fractions (*5*) and the stabilization of chelate complexes for different metals (*6*). A comparison of the dissociation of $H_2PO_4^-$ in water (*7*) and in different alcohol/water media (*8*, *9*) is presented in Table II.

We are concerned with providing a variety of operational pH values for solutions in alcohol/water media. The hydrogen electrode behaves satisfactorily in alcohol + water solvents, and a comparison of the emf obtained with that given by a glass electrode is often substantially uninpaired at solvent compositions below 90 mass % alcohols. A pH meter is also capable of giving reproducible emf values in alcohol/water solvents.

Experimental Section

The KH_2PO_4 and Na_2HPO_4 were NBS Standard Reference Materials 186 IC and 186 IIC; they were dried for 2 h at 120 °C. The 1-propanol was obtained from Aldrich Chemical Co., Inc. (spectral grade). Solvents were prepared by weighing the desired amount of double-distilled deionized water and adding the amount of 1-propanol to the desired mass percent composition. Then the calculated amount of KH_2PO_4, Na_2HPO_4, and NaCl was added to the desired concentration ranging from 0.1 to 0.001 ionic strength. Limited solubility in 50 mass % 1-propanol precluded the measurements of phosphate/NaCl solutions, and many of the cells misbehaved as a consequence of precipitation or freezing below room temperature. But no difficulty was experienced in obtaining equilibrium values of the emf before freezing occurred.

The preparation of electrodes and other experimental details were the same as in earlier work (*10*). Cells displayed good stability and the final emf at 25 °C, obtained after the measurements descending to −10 °C, usualy agreed with the initial values within 0.10 mV.

Results and Discussion

The cell used for the measurements can be represented by

$$\mathrm{Pt;Hg(g,\ 1\ atm)|KH_2PO_4}\ (m)\mathrm{,Na_2HPO_4}\ (m)\mathrm{,NaCl}\ (m)\mathrm{|AgCl;Ag}$$

where *m* is molality. The observed data, corrected to a partial pressure of hydrogen of 1 atm (101.325 kPa) as described earlier (*10*), are listed in Table III.

The mathematical relationship between the measured emf (*E*), the standard emf ($E°$), and the thermodynamic second dissociation constant of H_3PO_4 (pK_2) value was formulated as follows:

$$\mathrm{p}K_2' = \mathrm{p}K_2 - \beta I = \frac{(E - E°)F}{2.3026RT} + \log m + \frac{2AI^{1/2}}{1 + Ba°I^{1/2}}$$

where I is the ionic strength (for KH_2PO_4/Na_2HPO_4/NaCl(1:1:1), I is 5 *m*), and *A* and *B* are the constants of the Debye–Huckel theory, given in Table IV together with other physical constants of the mixed solvent needed for their evaluation. The ion-size parameters $a°$, which gave a satisfactory linear extrapolation,

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